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STUDY OF THE CHEMICAL STATE OF PALLADIUM IONS IN MULTILAYERS OF A CATALYTIC ACTIVITY

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ABSTRACT

Complexes of palladium (II) multilayers deposited on polyethyleneimine (PEI), polyacrylic acid (PAA) and humic acid (HA) fixed to glass are obtained by the method of the multilayer assemblylayer-by-layer «LBL». Films having from ten to forty polyelectrolyte layers (PEI-HA, PEI-PAA) comprising catalytically active metal palladium ions are obtained. X-ray photoelectron spectroscopy is used to study the nature of the latter and their distribution on the film exterior and interior surfaces. The possibility of using synthetic polycomplexes as active catalysts of the oxidation of o-xylene with oxygen is demonstrated. The catalytic systems of Pd (II)/(PAA-PEI)/glass and Pd (II)/(PEI-HA)/glass are investigated. The effect of the weight of the catalyst, the reactant concentration, the temperature, and the oxygen partial pressure on the oxidation of o-xylene at atmospheric pressure is investigated. The optimum process conditions are determined.

Keywords: multilayers, catalysts, polyethylene imine, polyacrylic acid, humic acid, Pd.

INTRODUCTION

More and more attention has been recently paid to compounds of original physico-chemical characteristics produced under uncommon conditions. The formulation of catalysts of a new generation of catalysts of good physico-chemical characteristics is an important problem of practical importance in modern chemical technology. The basis of such catalysts refers to active nanoparticles of metals of a variable valency incorporated in polylaers of polymer matrices, thus increasing the efficiency of their application and their selectivity [1 - 4]. One of the simple methods for such films preparation is the method of multilayer assembly, the so-called LBL method [5 - 9]. It provides producing ultrathin films of a designed thickness and composition from a great number of various systems. The assembly can be carried out on a charged surface of any geometry. The intentional binding of transition metal ions with functional groups of polymers in multilayers is of a special interest as it leads to the production of ultrathin films of a controlled thickness and surface possessing properties of importance for the practice.The heterogeneous catalysts thus obtained are active and selective and can be repeatedly used within several cycles of liguid phase oxidation. This is extremely important from economic and ecological points of view. The work in this direction is undoubtedly actual and of a practical importance. However, the surface and the nature of nanoparticles distribution in the composites multilayers are not well studied. The knowledge of these characteristics is necessary to identify the mechanism of the catalytic action.

This paper presents the results referring to the production of catalytically active composites on the basis of water soluble polyelectrolytes fixed on glass. They incorporate palladium ions. The latter distribution on the surface and inside the layers of the polymer composites is also studied.

EXPERIMENTAL

Materials

The study was carried out using poly(ethyleneimine) (PEI; $M_w 65D_a$), humic acid (HA) from brown coal of Oi-Karagai deposit, Kazakhstan (the total content of the acid groups referred to 6.4 mg-eq/g, that of carboxylic groups to 2.9 mg-eq/g, that of phenol hydroxyls to 3.5 mg-eq/g, that of carbonyl groups to 1.45 mg-eq/g), polyacrylic acid (PAA; M_w 450 kDa), hydrochloric acetic acid, sodium hydroxide, sodium tetrachloropalladate (II), Fluka acetic acid.

Preparation of the catalysts

Coating of layers. Plates of silicon and glass were immersed in concentrated sulphuric acid for 1 h and thoroughly washed with distilled water to a neutral value of pH. Then the plates were immersed in 0.25 M solution of NaOH for 10 min, washed with an excess amount of water and dried in a flow of nitrogen. The coating of multilayers on the surface of the plates was performed using solutions of polyelectrolytes in a buffer of a concentration of 0.3 mg/ml. The adsorption coating of polycation and polyanion layers on the support was performed by keeping the plates for 10 min in the corresponding solutions. The coating of every layer was followed by washing the plates with a buffer solution of an identical pH value. The multilayer composites obtained were stabilized by crosslinking within 1 h in a furnace at 125°C. The number of the layers varied from 10 to 40.

The incorporation of metal cations in the multilayers of the copolymer coated on glass was realized by immersing the samples in aqueous solutions of the corresponding salt of the metal (0,05 mol/l Na_2PdCl_4) of a chosen pH value (5.0, 8.5) and left to stand for 12 h. After saturation the copolymer multilayers were washed with the solvent.

The oxidation reaction of toluene with oxygen in the presence of a catalyst was carried out in a gradientless thermostated reactor connected to a calibrated burette. It was in a constant mixing mode.

Determination of the composites catalytic activity

Reaction of toluene oxidation was carried out in a glass in continuous gradient less thermo stated reactor of the “duck” type connected with a calibrated burette. The oxidation process was carried out for 1 h at 348 K and atmospheric pressure in acetonitrile medium. The volume of the reaction phase in all experiments was 10 ml, while the gas volume was 100 ml. The temperature was maintained with an accuracy of ±0.5°C using U-10 thermostat. The kinetic regime was provided by intensive shaking of the reactor (450 - 500 swingings a minute).The reaction rate was controlled by the oxygen consumption (Q_{O2} mole/l). The latter was calculated in regard to the volume of the reaction phase (0.001 l) of the reactor.

The catalyst surface was studied using K-ALPHA spectrometer. The samples were fixed to the standard holder of the device of a size of 60 mm x 60 mm using a conducting carbon scotch. A standard ion gun EXO6 with a holder providing azimuthal rotation was used for the spray profiling.

A source of a monochromatic radiation of a spot size of 400 μm was used to perform X-ray photoelectron spectroscopy. The onset of boost charge was compensated as the samples had a bad conductivity. A standard system of neutralization based on low power electrons (about 0.1 eV) and ions was used.

The spectra of the product samples were recorded on IR-spectrophotometer Specord 75 IR.

RESULTS AND DISCUSSION

The polymer metallic complexes are increasingly used as catalysts of oxidation of saturated and unsaturated hydrocarbons, alcohols and alkylbenzenes where oxygen, hydrogen peroxide, alkylhydroperoxides and other oxidants are used as oxidizing agents [10]. The main products of these reactions refer to the corresponding alcohols, ketones and hydroperoxides [11]. The processes of hydrocarbon oxidation by molecular oxygen catalyzed by complex compounds of transition metals are of great interest and are profitable from both economic and ecological points of view [12]. As oxygen is weak nonselective oxidant in many cases, a proper catalyst is necessary for its activation.

Silicates (glass) are known to possess mechanical strength and are resistant to grinding. That is why they can be used carriers of a polymer-metallic active phase. The ions of Cu (II), Ni(II), Fe(III), Pd(II), Pt(IV) form polymer-metallic complexes with the polyelectrolytes and have a catalytic activity in alkylaromatic and paraffin hydrocarbons oxidation and coal reduction. In this connection, it is envisaged to develop polymer compositions of polyelectrolytes and active metal ions, in particular, palladium ions. The mechanism of the metal ions incorporation in the films of PEI-HA and PEI-PAA fixed on glass is presented by the following scheme (Fig. 1).

The processes of interaction of catalytically active

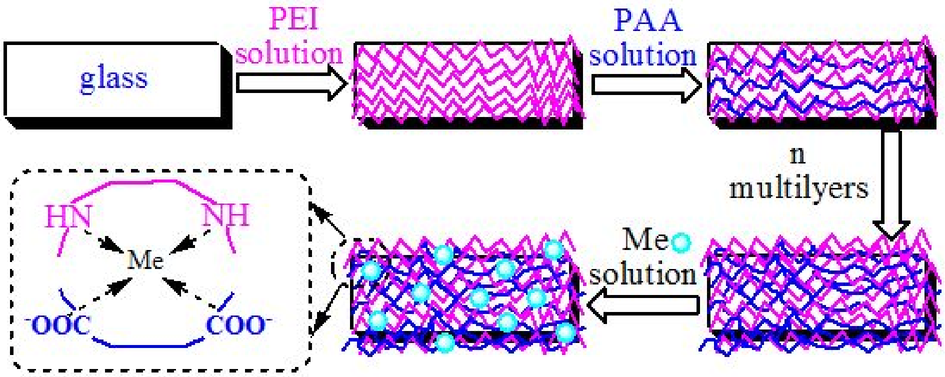


Fig. 1. A scheme of incorporation of metal cations into copolymer multilyers applied coated on onto glass.

metal ions with polyelectrolytes of a different chemical nature are studied and the corresponding optimum conditions of development of multilayers of a catalytic activity are defined [13].

Of special interest is to determine the nature of the different metal ions present on the surface of such multilayers and their distribution within the films. The preliminary analysis of the multilayer films containing palladium ions is performed by the method of X-ray photoelectron spectroscopy, XPS.

Films of 10, 20, 30 and 40 layers of PEI and humic acid as well as of PEI and PAA containing catalytically active metal ions in their compositions are obtained. The main physico-chemical characteristics of the films such as their thickness and roughness are studied earlier [13]. As shown the most active are the films based on PEI and PAA prepared by coating at pH=8.5 and pH=5.0 and a thickness of forty bilayers. The preliminary investigations of the catalytic activity of such metal containing polymer composites in the reaction of liguid phase oxidation of o-xylol show good results. The most active are the samples enriched mostly with PEI (pH = 8.5).

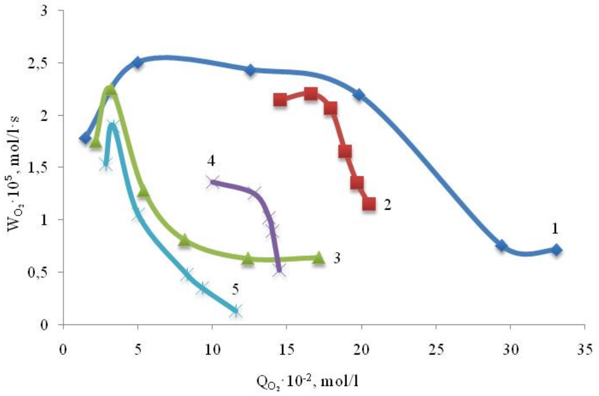


Fig. 2. The oxidation rate dependence of o-xylene on the testing catalyst with its five-fold use (from 1 to 5) (T = 348K, P_{atm} = 92.4 kPa,V(CH_3CN) = 1.0·10^{-3} l, C ($C_6H_4(CH_3)_2$) = 0.83 mol/l, mPd^{2+}/$(PEI\text{-}PAA)_{40}$(glass) = 0.5g).

The catalytic activity of Pd^{2+}/(PEI-PAA) and Pd^{2+}/(PEI-HA) in respect to the oxidation of o-xylol in an organic medium under mild conditions is studied. The effect of the catalyst, the reagent concentration, the temperature (in the range 333 - 348 K), and the partial pressure of oxygen on the oxidation process in monometric units at atmospheric pressure is studied. The optimum conditions of the process are determined.

Optimum temperature (T = 348 K) and catalyst mass (m_{cat} = 0.5 g) are determined for o-xylol oxidation using the composite catalyst Pd^{2+}/$(PEI\text{-}PAA)_n$.

The consumption of oxygen by the system is stated to increase with increase of the initial amount of o-xylol. It is shown that the 40-layer catalyst has the maximum rate or activity W_{O2} = 2.5·10^5 moL/L·s. Besides, it can be repeatedly used although a gradual decrease of its activity is observed.

According to the IR data obtained there are absorption bands characteristic for 1,2-substituted derivatives of the aromatic hydrocarbons, C-H groups of the aromatic ring, peroxide O-O and C-O-O groups, aldehyde C=O group bound to the aromatic ring as well as methyl groups at the aromatic ring (Table 1). The analysis performed provides to suggest that the products of o-xylol oxidation in a liquid phase at T = 348 K and P = 1 atm using Pd^{2+}/$(PEI\text{-}PAA)_{40}$/glass catalyst refer to o-xylolhydroperoxide and toluene aldehyde (Table 2).

Table 1. IR-spectra of the catalyzate of liquid phase oxidation of o-xylol on Pd^{2+}(PEI-PAA)$_{40}$/glass catalyst under optimum conditions (T=348 K, P=1 atm).

Bond group	Intensity of adsorption bands	Intervals of adsorption bands
$(-CH)_{ar}$	ν_{w}	3066.4 cm^{-1}
(C_6H_6)	ν_{tr}	1600 cm^{-1}, 1501.9 cm^{-1}
1,2 substituted $(-CH)_{ar}$	δ_{st}	748.2 cm^{-1}
$(O-O)_{st}$	ν_{w}	930.2 cm^{-1}
$(C-O-O)_{st}$	ν_{w}	1122.5 cm^{-1}
(C=O)	ν_{w}	2720.0 cm^{-1}, 1678.6 cm^{-1}, 1637.0 cm^{-1}
$(-CH_3)_{ar}$	ν_{st}	2952.0 cm^{-1}, 2863.0 cm^{-1}, 1444.7 cm^{-1}, 1423.9 cm^{-1}, 1377.2 cm^{-1}

Table 2. IR-spectra of the catalyzate of liquid phase oxidation of o-xylol on Pd2+(PEI-HA)40/glass catalyst under optimum conditions (T=348 K, P=1 atm).

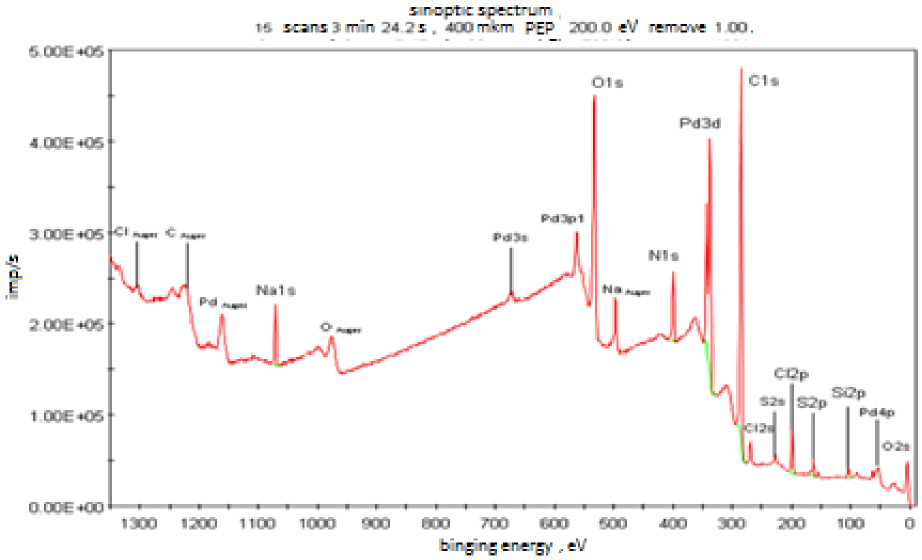
Bond group	Intensity of adsorption bands	Intervals of adsorption bands
$(-CH)_{ar}$	ν_{w}	3066.4 cm^{-1}
(C_6H_6)	ν_{tr}	1616.3 cm^{-1}, 1449.9 cm^{-1}
1, 2 substituted $(-CH)_{ar}$	δ_{st}	758.6 cm^{-1}
(C-OH)	δ_{st}	1496.7 cm^{-1}, 1387.6 cm^{-1}, 1250 cm^{-1}
$(C-O)_{st}$	ν_{st}	1496.7 cm^{-1}, 1387.6 cm^{-1}, 1250 cm^{-1}
$(O-O)_{st}$	ν_{w}	914.6 cm^{-1}
$(C-O-O)_{st}$	ν_{w}	1117.3 cm^{-1}, 1044.5 cm^{-1}
(C=O)	ν_{w}	2720.0 cm^{-1}, 1735.8 cm^{-1}, 1678.6 cm^{-1}
$(-CH_3)_{ar}$	ν_{st}	2936.5 cm^{-1}, 2884.5 cm^{-1}, 1496.7 cm^{-1}, 1449.9 cm^{-1}, 1387.6 cm^{-1}

The reaction equation may be presented in the form:

$$2CH_3C_6H_4CH_3 + 2O_2 \xrightarrow{k} CH_3C_6H_4CH_2OOH + CH_3C_6H_4CHO + H_2O.$$

The resistance of PEI-PAA copolymer layers to removal from the glass surface is reported in ref. [13]. The possibility of HA partial washing out from the glass surface is not excluded as there is a change of the color of the composite catalyst and a small decrease of its activity during its repeated use.

The distribution of the active metal in the layers of



Elements, at.%	
C	62.9
O	17.67
N	7.9
Pd	3.41
Cl	2.78
Na	1.9
S	1.8
Si	1.63

Fig. 3. XPS spectrum of multi–layer $(PEI\text{-}HA)_{40}$ catalyst.

the catalyst copolymer is not uniform. That is why it is necessary to study in detail the surface of the catalyst. This is done using XPS. Fig. 3 presents the XPS spectrum of $(PEI\text{-}HA)_{40}$ system and the elemental analysis data. The latter indicate that the content of palladium (II) in the multi-layer catalyst is of the order of 3.41 %.

More interesting information can be obtained from the analysis of the XPS spectrum. It provides a qualitative content of the elements in the multilayers of the catalysts obtained. These are, first of all, atoms of the components taking part in the multi assembly of the catalyst (carbon, oxygen, nitrogen, chlorine-ions) and the support used (sodium, silicon, sulphur ions). The XPS results show that the palladium ions in the multi layers have a different chemical nature. This is most clearly indicated by the data of the spectral analysis referring to the form of occurrence of palladium and carbon ions (Figs. 4, 5).

As Fig. 4 shows the XPS spectrum of the multilayer catalyst is singular. This indicates that the distribution

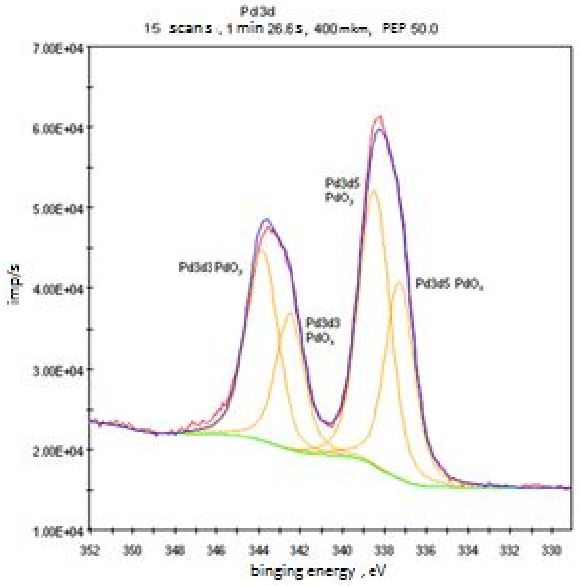


Fig. 4. XPS spectra for palladium ions.

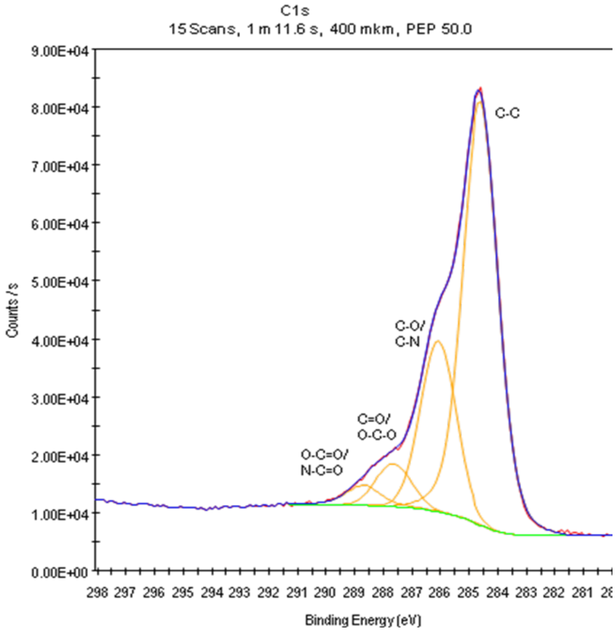
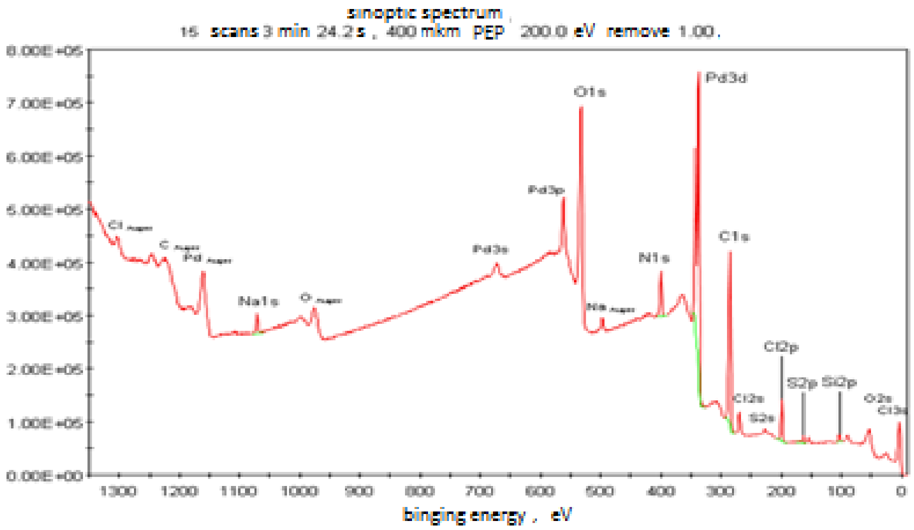


Fig. 5. XPS spectra for carbon ions.

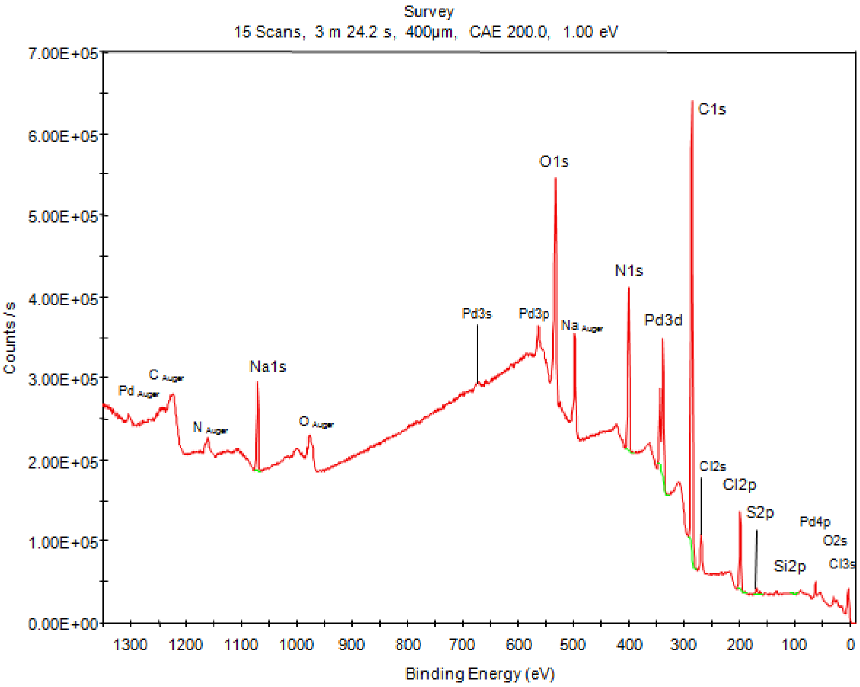


Elements, at.%	
C	63.63
N	14.12
O	13.2
Cl	4.18
Na	2.24
Pd	1.58
S	0.74
Si	0.31

Fig. 6. XPS spectrum of a separate fragment of the chemical state of palladium ions in PEI-HA multilayers.

of the palladium ions in the catalyst is uneven. This is evidenced by the difference in the state of Pd 3d³ in the PdOy and PdOx bonds. This difference is apparently due to the fact that both carboxyl and phenolic groups of the copolymer and humic acid take part in complexation with palladium [14]. The analysis of the spectrum (Fig. 6) indicates the nature of the chemical bonds of the carbon atoms in the polymer layers. They are N-C=O, O-C=O, O-C-O, C=O, C-N-, C-O, C-C. A more detailed characteristic of the palladium ions chemical state in multilayers can be seen in the fragment of RFS (Fig. 6). There are signals characterizing the participation of Pd $3p^1$, Pd $3p^3$ and O1s in Pd-O bond formation. This indicates that the adsorbed palladium ions take part in the formation of coordination bonds with the polyelectrolytes composing the multilayers.

Similar investigations are carried out with polymer matrices obtained on the ground of multilayers of poly-



Elements, at %	
C	51.65
O	23.64
N	8.08
Pd	7.39
Cl	4.6
Si	1.96
S	1.39
Na	1.28

Fig. 7. XPS spectra for Pd^{2+}/(PEI-PAA)/glass systems at pH = 8.5.

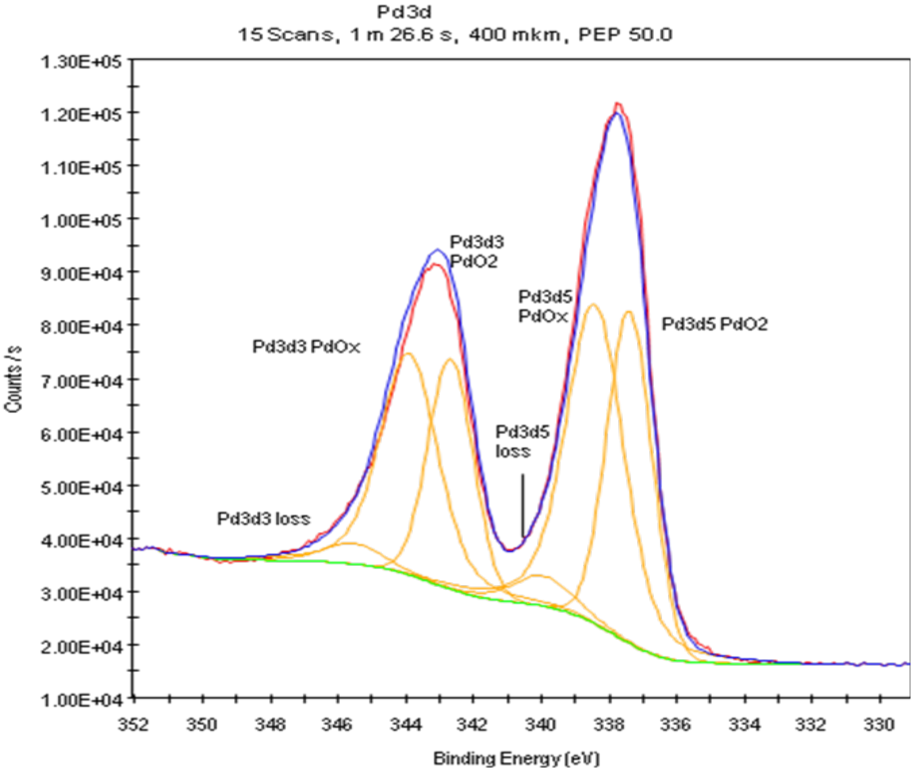


Fig. 8. XPS spectra for Pd^{2+}/(PEI-PAA)/glass systems at pH = 5.

acrylic acid and polyetylenimine containing palladium ions. They are obtained by coating at different values of pH. The results obtained are illustrated in Figs. 7 and 8.

The spectra of Pd/(PEI-PAA)/glass system at different values of pH contain a qualitative pattern of the chemical state of the elements in the multilayers and quantitatively characterizes their content. The elemental analysis shows that the content of palladium is greater at pH = 5 than that at pH = 8.5.

As it should be expected, the competing interactions of the metal ions with macromolecules of a different nature and/or a different density of charges in PEML will strongly depend on pH of the medium. The film of PEI-PAA coated at pH=5.0 contains more segments of the polyacid and a comparatively greater amount of free (not bound to aminogroups) carboxylic groups in a "loopy" conformation of the polyacid than that of PEI aminogroups [13]. In this case, the metal cations bind preferably with the carboxylic groups [15, 16]. The polyacrilic acid is in a completely ionized form at pH = 8.5 and forms strongly cross-linked thin layers not accessible for binding with Me^{2+}, while PEI having a relatively low charge density is applied in the form of thick layers with a "loopy" conformation of free amino groups able to coordinate metal cations [13]. It should be noted that polyethylenimine as a complex forming ligand is weaker under such conditions than polyacrylic acid and the palladium ions content on the multilayers surface will be less at pH = 8.5 than that at pH = 5. Both polymers form thin cross-linked layers at neutral pH and which is why the amount of the palladium ions is less.

The state of the palladium ions in these systems is indicated by the spectra of the separate fragments related to the forms of occurrence (Figs. 9, 10). It is evident that the forms of occurrence differ from those in PEI-HA system. The presence of Pd $3d^3$ in PdO_x and Pd $3d^3$ in PdO_2 as well as Pd $3d^5$ in PdO_x and Pd $3d^5$ in PdO_2 are clearly outlined. The comparison of the spectra of the chemical state of palladium ions in PEI-HA and PEI-PAA confirms this supposition (Fig. 10).

The state of palladium in PEI-PAA sample at pH = 8.5 differs from those of the other two samples. There are no less than two different sates of palladium atoms in the samples of PEI-HA and PEI-PAA at pH = 5.0. Hence, it follows that as a complex former, palladium can react with the functional groups of the polylayer reagents following a donor–acceptor mechanism although the formation of electrostatic and hydrogen bonds with the

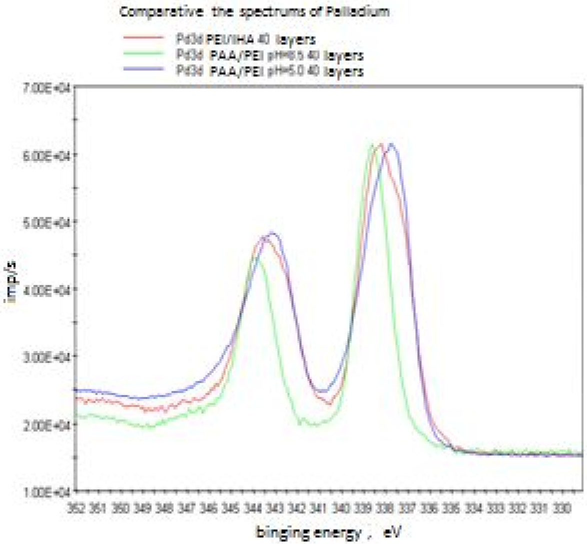


Fig. 9. Fragments of XPS spectra related to the chemical state of palladium ions in multilayers for Pd^{2+}/(PEI-PAA)/glass systems at pH = 8.5.

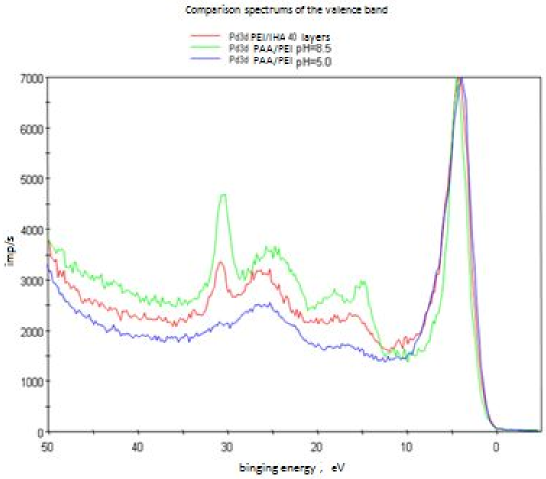


Fig. 10. A comparative spectrum of general state of palladium ions in multilayer.

polyelectrolytes is not excluded. Therefore, the chemical state of palladium ions in the multilayers and on the surface may be different.

Fig. 11 presents the spectra of the valence band of the systems Pd^{2+}/(PEI-HA)/glass and Pd^{2+}/(PEI-PAA)/glass which differ in their parameters. This fact verifies the different chemical state of the elements in the multilayers.

As expected, the structure of the valence band of PEI-PAA sample differs at pH = 8.5 from those of the other two samples. One of the important questions arising in the course of multilayer films analysis refers to the surface distribution of the metal ions. It is especially important in explaining the catalytic activity observed.

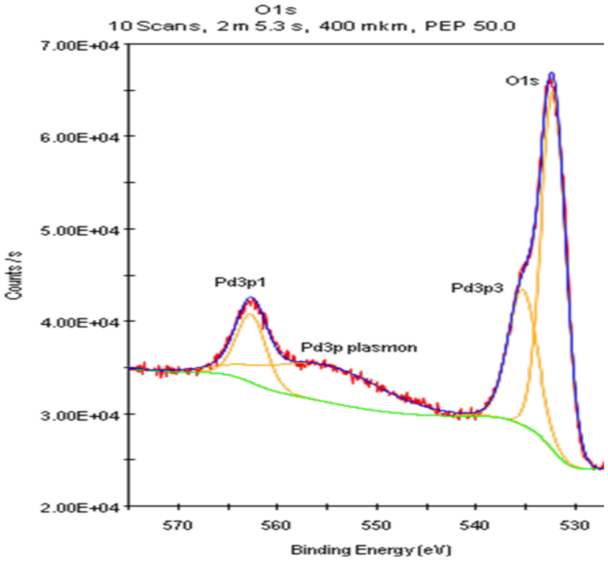


Fig. 11. Spectra of valence band of the obtained multilayer catalysts.

An attempt is made to investigate the distribution of palladium ions in the synthesized multilayers by using XPS. A concentration profile is obtained to determine the change of the elements concentration with thickness variation. An azimuthal rotation is used to obtain a uniform bottom of the etching crater. The etching itself is carried out by ionized Ar atoms in a monatomic regime at a power of 500 eV. The regime of a “momentum picture” and the spectrometer 128-canal detector are used to obtain the data. The general tendency observed shows that the concentration of palladium and carbon decreases considerably with the thickness increase. It is worth adding that there is glass (silicon, sodium, calcium oxides) under the surface film of the polymer/complexes in all samples.

The XPS spectra of the concentration profiles of the chemical elements in the films show a maximum concentration of the palladium ions on the multilayers surface in all cases. The concentration of these ions as well as that of nitrogen and chlorine atoms decreases in the course of moving to the support. This indicates the fact that the palladium ions content in the films bilayers decreases with decrease of the polymer matrices layers. Concentration of silicon and oxygen atoms (the material of the support) naturally grows, when going from the top layer to the surface of the carrier.

The method is applied for the first time for the samples studied. The authors assume that the thickness of the polymer layers formed in a multilayer catalyst and the distribution of the metal in them will differ depending on pH.

CONCLUSIONS

The method of layer-by-layer LBL assembly helped to produce and study some properties of palladium catalysts coated on polylayers of polyethylene imine and polyacrylic acid. The nature of palladium ions in the multilayers of these catalysts was studied by XPS.

The study of the surface of the catalyst multilayers obtained indicates that the chemical nature of the palladium ions inside and on the surface of the bilayers is different. The palladium ions of the inside layers form coordination bonds with the functional groups of the polyelectrolytes composing the bilayers. On the multilayers surface the metal coordinates probably with active centres of the upper layer and with chlorine ions filling the free ligand space of the palladium ion according to its coordination number. The palladium different forms have most probably different catalytic properties but it is difficult to identify whose activity is greater.

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